## Active Filtration of Phosphorus in Ca-Rich Hydrated Oil Shale Ash Filters: The Effect of Organic Loading and Form of Precipitated Phosphatic Material

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Abstract : For small-scale wastewater management, the treatment wetlands (TWs) as a low cost alternative to conventional treatment facilities, can be used. However, P removal capacity of TW systems is usually problematic. P removal in TWs is mainly dependent on the physico-chemical and hydrological properties of the filter material. Highest P removal efficiency has been shown trough Ca-phosphate precipitation (i.e. active filtration) in Ca-rich alkaline filter materials, e.g. industrial byproducts like hydrated oil shale ash (HOSA), metallurgical slags. In this contribution we report preliminary results of a fullscale TW system using HOSA material for P removal for a municipal wastewater at Nõo site, Estonia. The main goals of this ongoing project are to evaluate: a) the long-term P removal efficiency of HOSA using real waste water; b) the effect of high organic loading rate; c) variable P-loading effects on the P removal mechanism (adsorption/direct precipitation); and d) the form and composition of phosphate precipitates. Onsite full-scale experiment with two concurrent filter systems for treatment of municipal wastewater was established in September 2013. System's pretreatment steps include septic tank (2 m2) and vertical down-flow LECA filters (3 m2 each), followed by horizontal subsurface HOSA filters (effective volume 8 m3 each). Overall organic and hydraulic loading rates of both systems are the same. However, the first system is operated in a stable hydraulic loading regime and the second in variable loading regime that imitates the wastewater production in an average household. Piezometers for water and perforated sample containers for filter material sampling were incorporated inside the filter beds to allow for continuous in-situ monitoring. During the 18 months of operation the median removal efficiency (inflow to outflow) of both systems were over 99% for TP, 93% for COD and 57% for TN. However, we observed significant differences in the samples collected in different points inside the filter systems. In both systems, we observed development of preferred flow paths and zones with high and low loadings. The filters show formation and a gradual advance of a "dead" zone along the flow path (zone with saturated filter material characterized by ineffective removal rates), which develops more rapidly in the system working under variable loading regime. The formation of the "dead" zone is accompanied by the growth of organic substances on the filter material particles that evidently inhibit the P removal. Phase analysis of used filter materials using Xray diffraction method reveals formation of minor amounts of amorphous Ca-phosphate precipitates. This finding is supported by ATR-FTIR and SEM-EDS measurements, which also reveal Ca-phosphate and authigenic carbonate precipitation. Our first experimental results demonstrate that organic pollution and loading regime significantly affect the performance of hydrated ash filters. The material analyses also show that P is incorporated into a carbonate substituted hydroxyapatite phase. Keywords : active filtration, apatite, hydrated oil shale ash, organic pollution, phosphorus

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